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A Study of Irradiation Induced Active Sites on MgO Using Electron Paramagnetic Resonance

by

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Introduction

Previous work has shown that the catalytic activity of MgO powders can be enhanced by ultraviolet irradiation provided the catalyst has not been completely degassed (1). The present investigation includes a study of the induced catalytic activity and electron paramagnetic resonance (EPR) spectra on the same sample. It will be shown that there is a correlation between the V_1-center and the irradiation induced catalytic activity.

The V_1-center is defined in Slide #1 as a hole trapped at an anion adjacent to a positive ion vacancy. For it to be formed, several conditions must be satisfied including charge compensation for the positive ion vacancy, a quanta of light having sufficient energy to free an electron, and an electron trap. Irradiation removes electrons from the valence band, and the resulting electron hole (called simply a hole) is then free to move through the lattice until it is trapped at the positive ion vacancy. This center now has an unpaired electron which may be detected by EPR techniques.

The resonance condition for free electrons is described in Slide 2. In the absence of an external magnetic field, the lowest energy level is twofold degenerate since the spin states +1/2 and -1/2 are indistinguishable. In a magnetic field, however, the degeneracy of the level is removed and two energy levels are resolved. The difference in energy between these states is proportional (related by the g-value) to the magnetic field. If one were to irradiate the sample with electromagnetic waves having energy $h\nu$, then transitions could be induced from the lower to the higher energy level. In practice the sample is irradiated at about ten thousand megacycles and the magnetic field is swept. At a certain field the resonance condition is satisfied, resulting in energy absorption which can be detected and traced out on a recorder.

When the electron is in a crystalline field the g-value is, in general, a tensor. A paramagnetic center having an electron spin S = 1/2, in axial symmetry will have a g-value for each angle which the symmetry axis makes with the magnetic field vector. In a powder sample, where

all angles are possible, the expected absorption spectra is shown in Slide 3. The derivative curve is usually plotted for instrumental reasons. The spectra of a UV irradiated, iron doped sample is shown in the same slide.

One of the advantages in studying MgO is that a substantial amount of EPR work has been carried out on single crystals by Wertz, Low, and other investigators. Wertz (4) has identified the V_1-center spectrum with $g_{\parallel} = 2.0032$ (magnetic field along the symmetry axis) and $g_{\perp} = 2.0385$ (magnetic field perpendicular to the symmetry axis). The lines broaden at temperatures higher than 77°K and decay out upon heating the samples to 100° for a few minutes.

Experimental Data and Discussion

These g-values observed by Wertz are shown on Slide 4, which includes the spectrum of an MgO catalyst degassed at 290°C and irradiated with 2537Å UV. From the similarity in the spectra one may conclude that the center observed in the powder is of a V_1 type. Strictly speaking, a V_1-center cannot exist at the surface because of the absence of neighbor atoms on one side of the interface. It is not clear whether a V_1-type center, formed by a missing surface Mg^{++} atom, would have a significantly different g-value than one in the bulk. While hydrogen and oxygen have a marked effect on the iron doped sample, these gases change the spectrum of the "pure" sample only slightly.

The purpose of the subsequent discussion will be to present data showing that this V_1-center and the irradiation induced catalytic activity for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ respond in a similar manner to: (1) degassing the sample at 290°C and 500°C; (2) thermal decay at -79°C, 0°C, and 30°C; (3) 2537Å UV as a function of time; and (4) several wavelengths of UV light. The samples used were reagent grade MgO which had been mixed with water to form a paste and then extruded to form pellets approximately two millimeters in diameter. All catalytic measurements were made at -78°C and EPR measurements at about -196°C. The reaction rates are reported as a first order rate constant.

When the samples were degassed at 290°C and then irradiated with 2537Å UV light, the catalytic activity increased about tenfold and the V_1-center spectrum appeared. The catalytic activity of the samples degassed at 500°C and irradiated showed no change in activity and no V_1-center spectrum. The effect of degassing at 290°C is to partially remove surface and interlattice hydroxyl groups. The remaining hydroxide ions probably act as charge compensating centers for the positive ion vacancies. Their role as electron acceptors during irradiation is also possible. When these hydroxyl groups are removed by degassing at higher temperatures, the cation vacancies diffuse out to the surface and no V-centers can be formed upon irradiation.

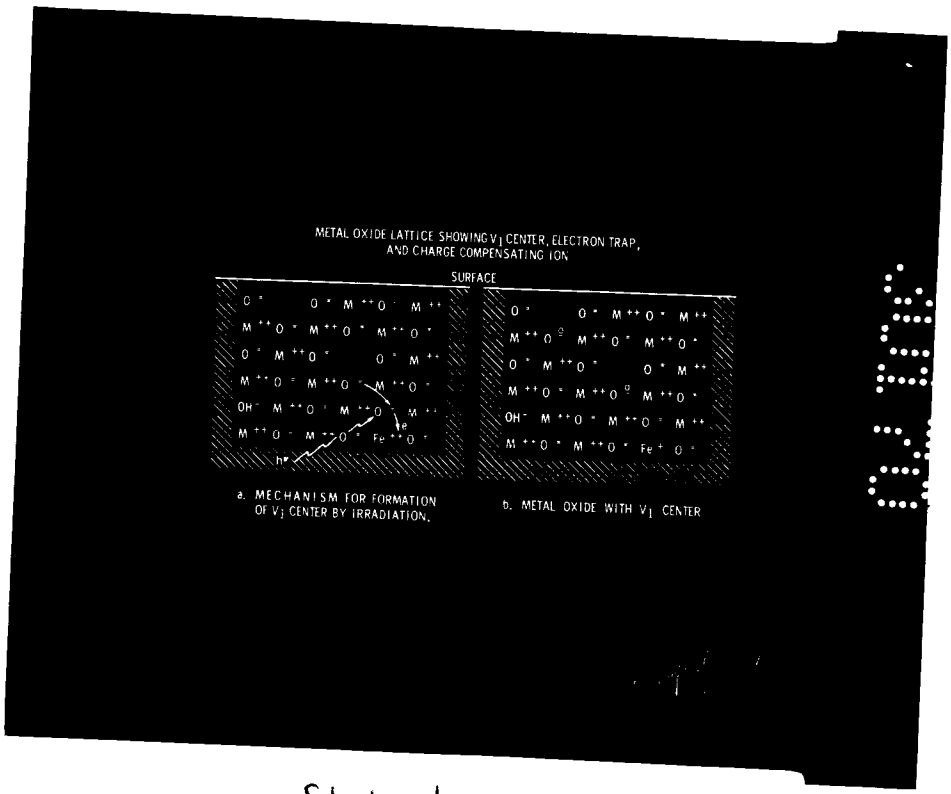
References

1. Lunsford, J. H. and Leland, T. W., J. Phys. Chem., 66, 2595 (1962)

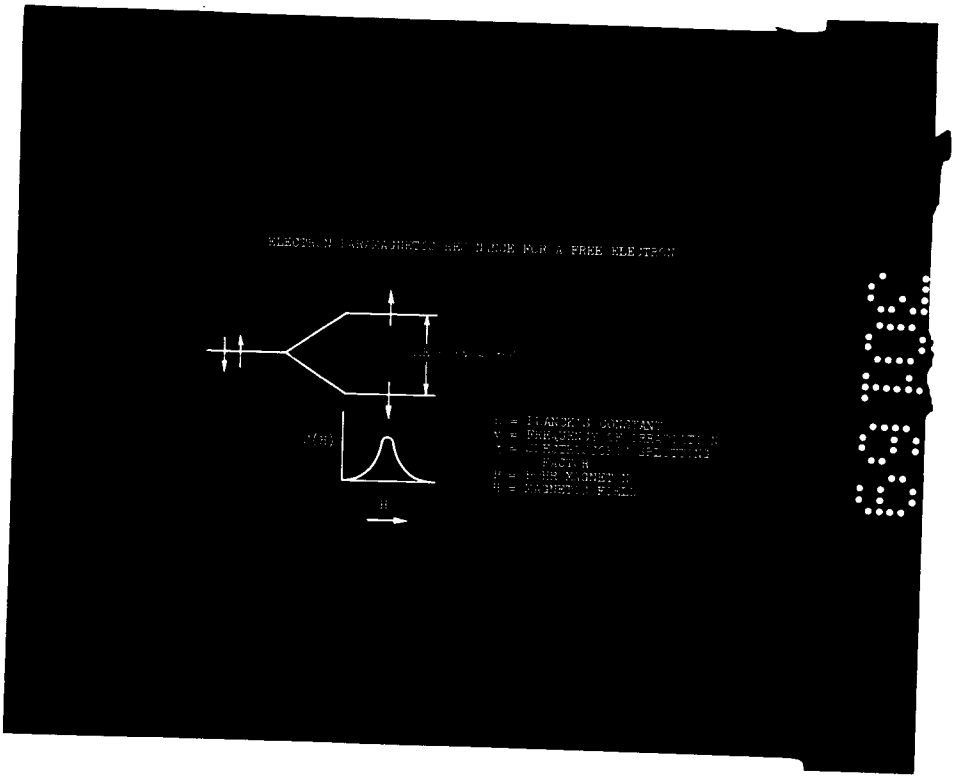
2. Peria, W. T., Phys. Rev., 112, No. 2,423 (1958)

3. Soshea, R. W., Dekker, A. and Sturtz, J. P., J. Phys. Chem. Solids 5, 23 (1958)

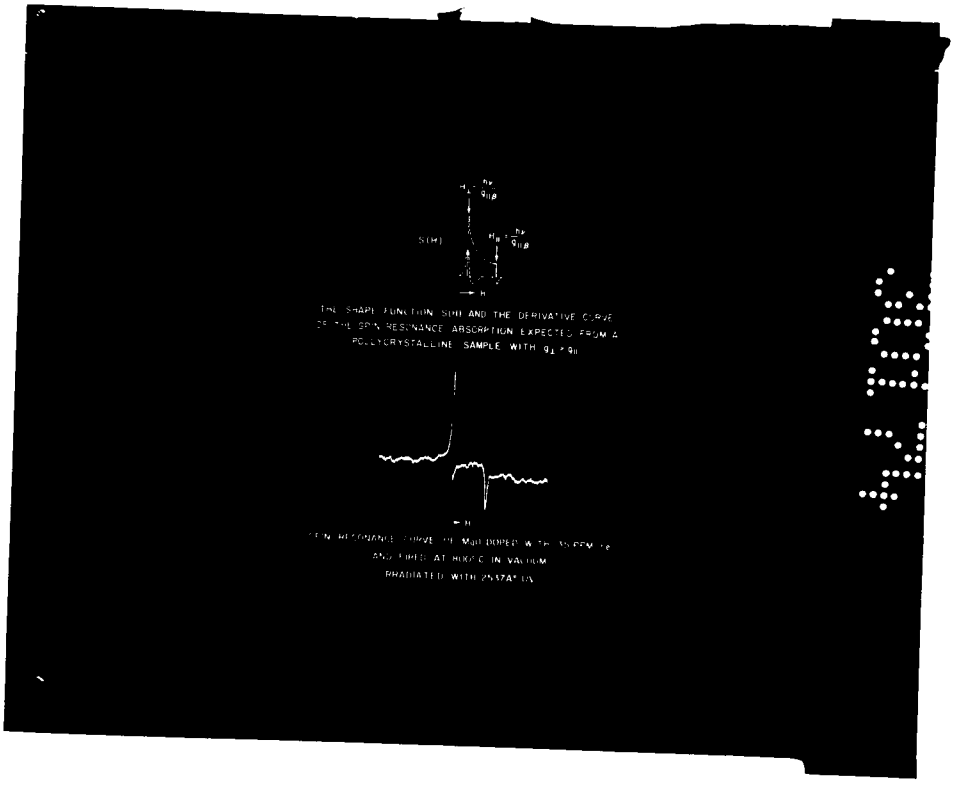
4. Wertz, J. E., Auzins, P., Griffiths, J. H. E. and Orton, J. W., Faraday Soc. Disc., 28, 136 (1959)


METAL OXIDE LATTICE SHOWING V_1 CENTER, ELECTRON TRAP, AND CHARGE COMPENSATING ION
SURFACE
a. MECHANISM FOR FORMATION OF V_1 CENTER BY IRRADIATION.
b. METAL OXIDE WITH V_1 CENTER

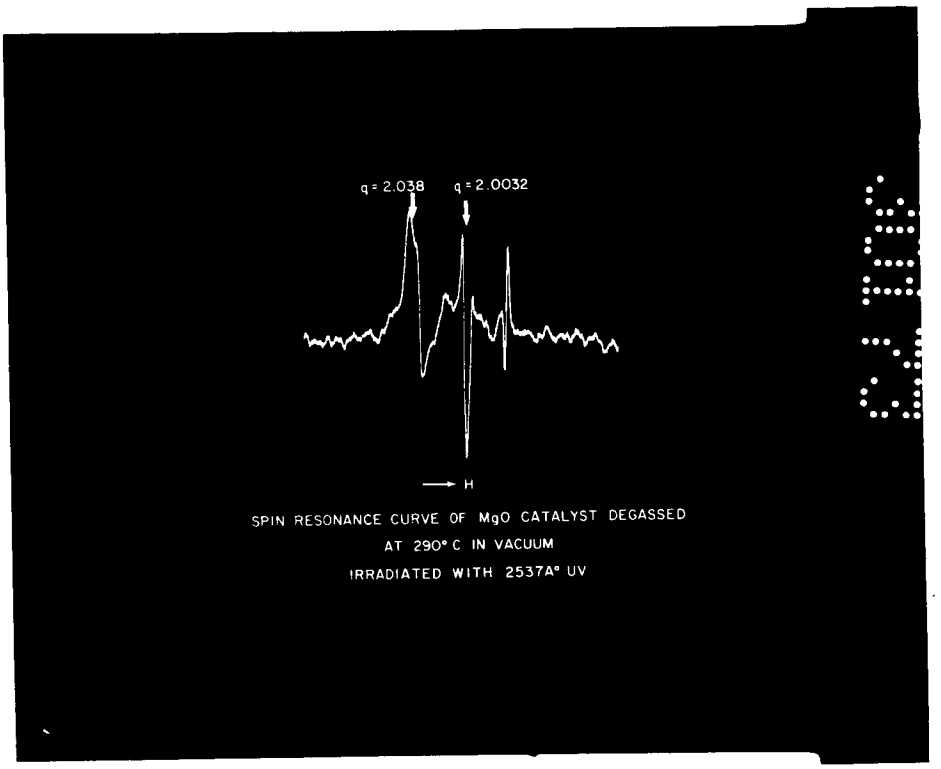
Slide 1



Slide 2

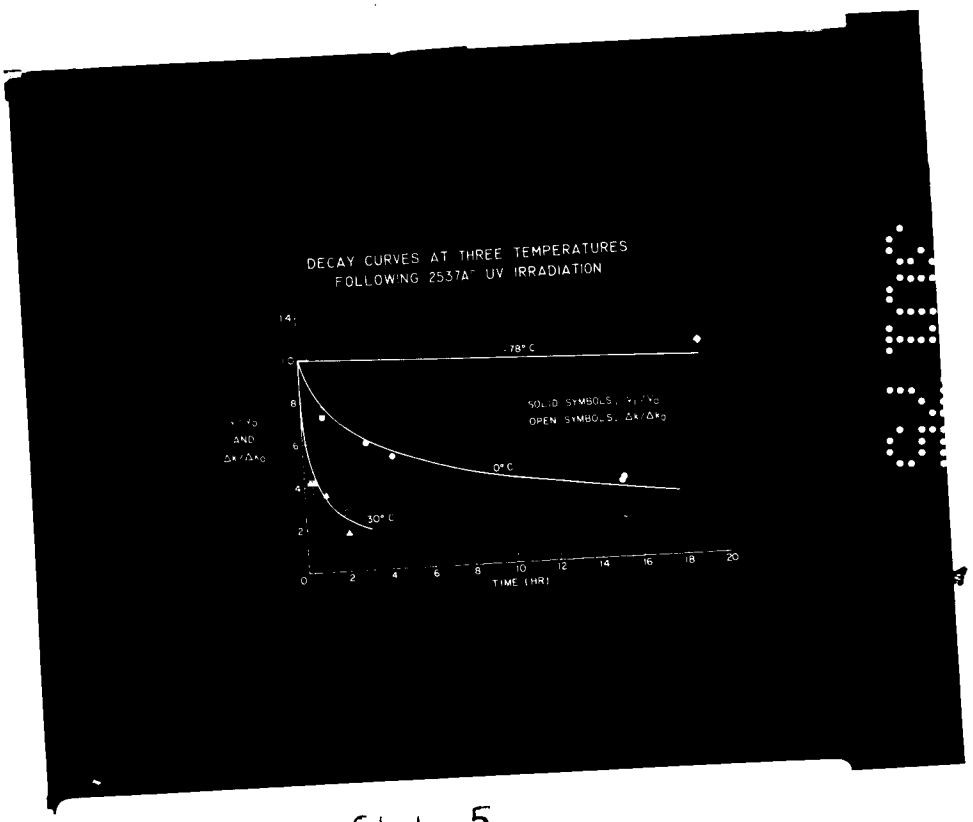


Slide 3

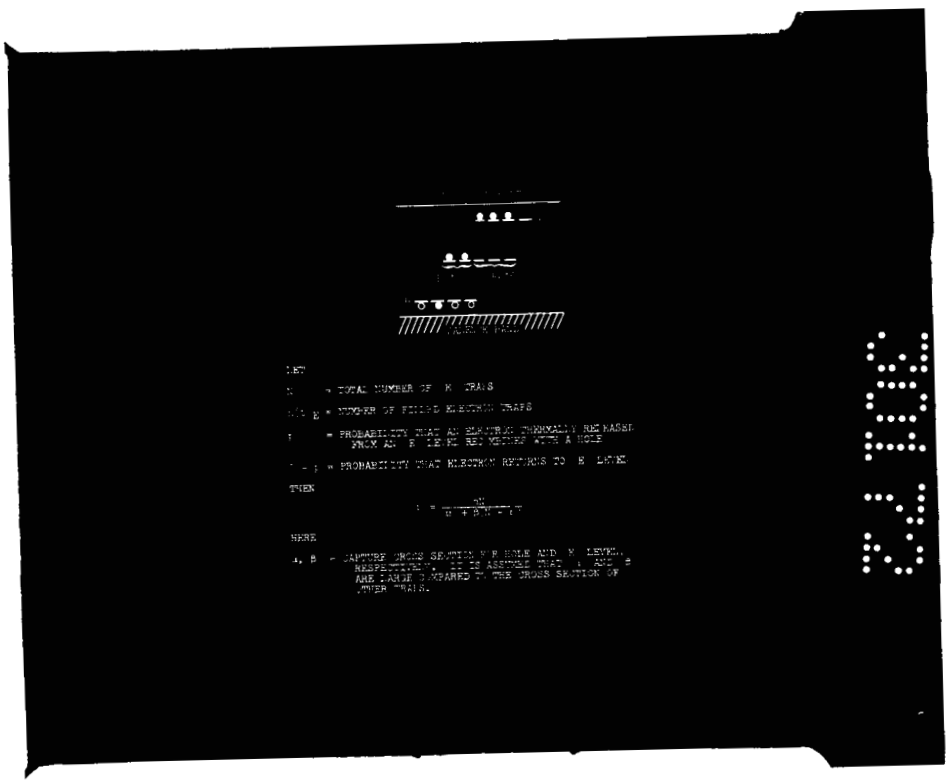


SPIN RESONANCE CURVE OF MgO CATALYST DEGASSED
AT 290° C IN VACUUM
IRRADIATED WITH 2537A° UV

Slide 4


DECAY CURVES AT THREE TEMPERATURES
FOLLOWING 2537A° UV IRRADIATION
-78° C
SOLID SYMBOLS, X/X0
OPEN SYMBOLS, ΔX/ΔX0
0° C
30° C
TIME (HR)

Slide 5



Slide 6

THE DECAY IS THEN DETERMINED BY

$$\frac{dn}{dt} = \gamma p n$$

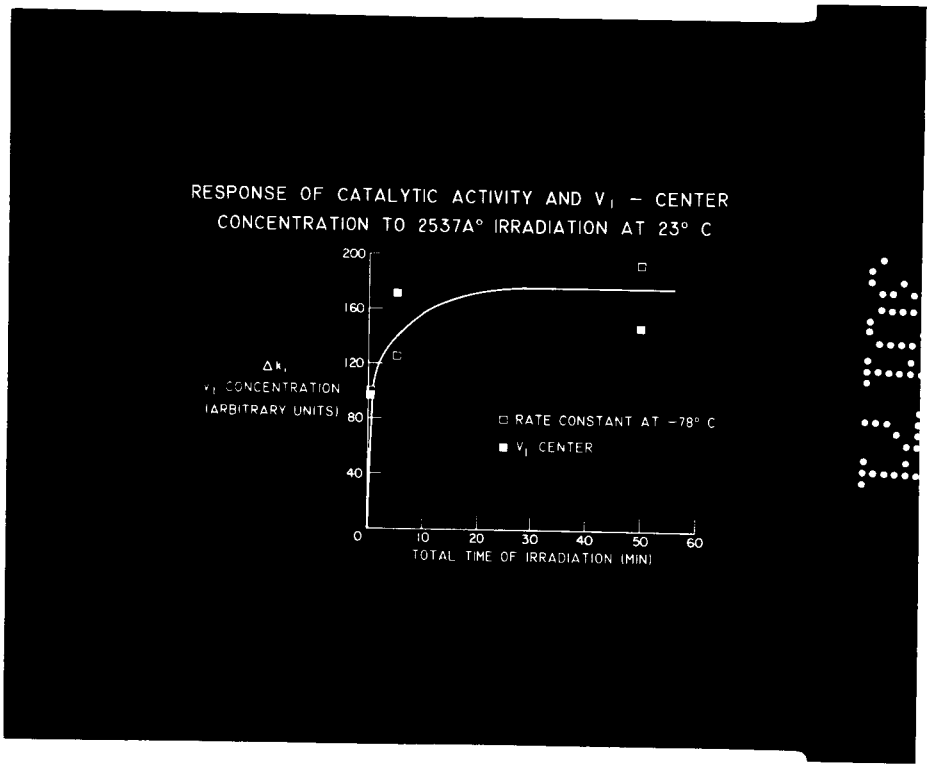
WHERE γ IS A PROPORTIONALITY CONSTANT DEPENDING ON TEMPERATURE.

SOLVING GIVES

$$t = C_1 \log[n/n(0)] + (C_2/n)[1 - n/n(0)]$$

WHERE $C_1 = (\beta - \alpha)\nu\alpha$ and $C_2 = \beta N/\gamma\alpha$

Slide 7


RESPONSE OF CATALYTIC ACTIVITY AND V_1 – CENTER CONCENTRATION TO 2537A° IRRADIATION AT 23° C
200
160
120
80
40
0
Δκ, V_1 CONCENTRATION (ARBITRARY UNITS)
10
20
30
40
50
60
TOTAL TIME OF IRRADIATION (MIN)
□ RATE CONSTANT AT −78° C
■ V_1 CENTER

Slide 8

EFFECTS OF IRRADIATION WITH UV LAMPS OF THREE

DIFFERENT MINIMUM WAVELENGTHS LIGHT

DURATION OF IRRADIATION: 15 MIN.

	V_1	$\Delta k \times 10^4$
1. SL 3660 WITH FILTER, CONTINUOUS SPECTRA FROM 3200 TO 3400 A°	0	-0.3
2. SL 3660 WITHOUT FILTER, INCLUDES LINES AT 3125 A° AND 3131 A° BUT NOT 2537 A°	2	1
3. SL 2537 A°	29	29

Slide 9